tion of the sample gas with something in the sample inlet system, ion source or analyzer system of the spectrometer. If adsorption of some species is the primary process on which these ions depend and the adsorbing surface is only partially covered at low pressures, a first-order pressure dependence is expected. At higher sample pressures the surface should be completely covered, with the resulting effect being the apparent zero-order dependence observed. Support of this thesis was given by an experiment in which the sample gas pressure in the source was greatly reduced. At pressures from $^1/_{500}$ to $^1/_{200}$ of the normal operating pressure, the ion currents at lower electron accelerating voltages varied directly as the pressure.

It is interesting to note that the initial break of the ionization efficiency curves for all the ion fragments exhibiting an apparent double break was 12.5 ± 0.5 volt for fluoride fragments and 11.5 ± 0.5 volt for the chloride fragments. This small variation suggests that these fragment ions may be of thermal origin and not primarily due to electron bombardment of gaseous molecules.

Figure 3 shows the Cr^+ and $CrOF^+$ curves as they appeared at various pressures. The upper number of each Cr^+ curve is the relative ion current for 45-volt electrons. The lower number is the value at 25 electron volts. The number on the $CrOF^+$ curve is the relative ion current for 45-volt electrons.

It would be tempting to interpret these results in terms of the bond strengths in molecular or ionic chromyl halides. However, the paucity of ionization potential data for CrO^+ or CrX^+, coupled with the uncertainties involved in interpreting such data as presented in Figs. 2 and 3, make any such attempts tenuous. It is apparent that no simple assumptions can be made which represent the processes occurring in the mass spectrometer ion source. While the results listed in Table I appear to have some consistency, their meaning in terms of thermodynamic properties in these molecules is clouded by the several likely processes which may be occurring.

Attempts to measure ionization efficiencies of the chlorofluoride fragment ions were unsuccessful, except for the parent ion. The value of 14.0 ± 0.2 volt was obtained for the appearance potential from a measurement on a mixture containing very little chloride. The amount of chlorofluoride present was large enough to give reliable results, and the very small amount of $CrOCl_2^+$ from the chloride did not interfere.

It was thought that the appearance potential curves for some of the ions of a mixture of all three compounds might exhibit two or more "breaks" because of the probable difference in appearance potential of the ions which are common fragments of two or all of the compounds. In the course of work reported here, no such breaks were observed on any mixture.

AMES, IOWA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Iron(III) Complexes in Non-aqueous Solvents. I. The Solvolysis and Chloride Complex Constants in N-Methylacetamide

BY WARREN L. REYNOLDS AND ROGER H. WEISS

RECEIVED OCTOBER 31, 1958

Spectrophotometric measurements yielded values of 1.4×10^{-3} mole liter^{-1} for the first solvolysis constant of Fe^{+3} and 7.5×10^2 and 13 liter mole^{-1} for the stepwise formation constants of $FeCl^{+2}$ and $FeCl_2^+$, respectively, in N-methylacetamide. The molar extinction coefficients at 365 mμ of FeS^{+2} (where S^- is the solvent anion), $FeCl^{+2}$ and $FeCl_2^+$ were found to be 1.8×10^3, 1.9×10^3 and 9.3×10^3, respectively. The average latent heat of vaporization of N-methylacetamide over the temperature interval from 115 to 205° was 14.2 kcal. mole^{-1}.

Experiments, preliminary to an investigation of the kinetics of the Fe(II) + Fe(III) isotope exchange reaction in the solvent N-methylacetamide (NMA), showed that Fe^{+3} formed complexes with the anions of various strong mineral acids in this solvent. In Fig. 1 are shown spectra of anhydrous $FeCl_3$ dissolved in NMA in the presence of 0.1 *M* hydrochloric, perchloric and sulfuric acids and in the absence of any added acid. Presence of water up to at least one molar had no appreciable effect on these spectra. Apparently complexes between Fe^{+3} and the various anions are formed which have different absorption spectra. Therefore, before the rate constants for the isotopic exchange of iron between Fe(II) and the various Fe(III) complexes could be determined, it was necessary to determine the association constants of some of these complexes and to determine the solvolysis constant of Fe^{+3} in NMA.

The solvent NMA was chosen because it could be obtained in relatively anhydrous condition (water concentration less than 0.002 *M*) and because of its high dielectric constant.

Experimental

Reagents.—Iron(III) chloride was prepared by passing dry Cl_2 gas at room temperature through iron powder in the presence of a trace of moisture. The product was analyzed iodometrically and found to contain 96.8% $FeCl_3$. The main impurity probably was water; the amount of water introduced with the $FeCl_3$ in making a 0.1 millimolar solution of Fe(III) was thus much less than the minimum water content which could be detected by a Karl Fischer titration.

Hydrochloric acid solutions were prepared by passing dry HCl gas[1] into NMA. The solutions were standardized by diluting an aliquot at least twofold with water and titrating with standard NaOH using phenolphthalein as indicator.

Standard NaCl solutions were prepared by dissolving an-

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[1] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., p. 117.

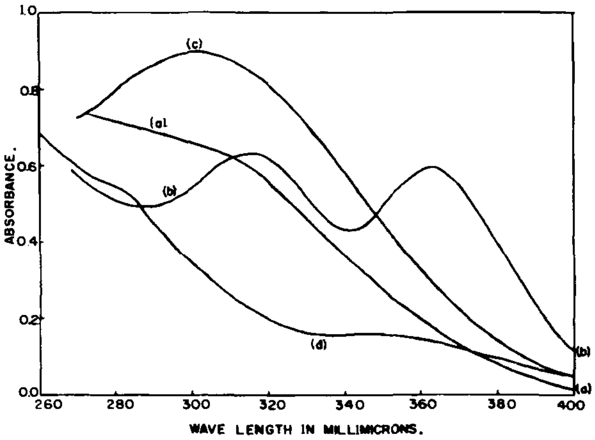

Fig. 1.—[FeIII] = 8 × 10^{-5} *M:* (a) 0.1 *M* H_2SO_4; (b) 0.1 *M* HCl; (c) 0.1 *M* $HClO_4$; (d) no acid added; cell length 1.00 cm.

hydrous Mallinckrodt analytical reagent in a known volume of solution.

The anhydrous solvent was prepared by a slight modification of a method recommended by Mr. Laurance Knecht[2] of this department. Gaseous methylamine was distilled into excess glacial acetic acid. The resulting solution of methylammonium acetate in acetic acid was refluxed overnight, followed by elimination of the major portion of the water produced in the amide formation by distillation at atmospheric pressure until the temperature rose to approximately 120°. Concentrated sulfuric acid then was added to combine with any unreacted methylamine and distillation was continued under reduced pressure. The first portions of distillate containing large amounts of acetic acid were discarded. The acetic acid content in the remaining distillate was reduced to less than polarographically detectable amounts by shaking with calcium oxide or with potassium carbonate and then distillation at reduced pressure. The resulting solvent containing some water was polarographically and spectrophotometrically pure. Distillation from phosphorus pentoxide under reduced pressure introduced a small amount of an impurity reducible at a dropping mercury electrode at −2.2 v. relative to a saturated calomel electrode. This material apparently did not affect the spectrum of the pure solvent or the spectra of the Fe(III)-Cl^- complexes. The solvent was analyzed for water by a Karl Fischer titration and found to contain less than 0.002 molar water.

Apparatus.—A Cary model 11 recording spectrophotometer was employed for scanning of spectra. A Beckman model DU spectrophotometer was employed for absorbance measurements at constant wave length. Since neither instrument was thermostated at the desired temperature and since the solvent froze at approximately 29°, it was necessary to warm a sample somewhat before placing it in the cell compartment. Thus the temperature of a sample was never accurately known. This affected measurements in two ways: namely, through the effect of temperature on the equilibrium constants involved and through the effect of an appreciable volume change on concentrations and resulted in an error of about 6% in the proportionality constant between absorbance and Fe(III) concentration.

Procedure.—Stock $FeCl_3$, NaCl and HCl solutions were added to solvent in such amounts as to give the desired concentrations of Fe(III), Cl^- and H^+. The absorbances of solutions in 1-cm. glass-stoppered silica cells were measured at 351.5 and 363 mμ. Absorbance measurements were made at 351.5 mμ because this wave length was apparently an isosbestic point for the two species $FeCl^{+2}$ and $FeCl_2^+$, and a change of absorbance at this point indicated the appearance of additional forms of Fe(III) in solution. The absorbance measurements at 363 mμ were used to calculate the molar extinction coefficients and equilibrium constants desired.

Results and Discussion

Latent Heat of Vaporization.—The boiling point of NMA at 24 mm. pressure was 115°. Using the value of 205° for the normal boiling point[3] the average heat of vaporization calculated from the integrated Clausius–Clapeyron equation was 14.2 kcal. $mole^{-1}$. The value calculated from the data in Heilbron[3] for the temperature interval 140.5 to 205° was 13.1 kcal. $mole^{-1}$. This value is significantly greater than the value for water and probably results from the larger dipole moment of NMA as compared to water.

Fe(III) Complexes Present.—Iron(III) spectra at three different HCl concentrations and an Fe(III) spectrum in the absence of added acid are shown in Fig. 2. The presence of an isosbestic point at approximately 351 mμ suggests that only two Fe(III)–Cl^- species are predominant in the concentration range 0.015 to 0.10 *M* HCl. These were assumed to be $FeCl^{+2}$ and $FeCl_2^+$. The Fe(III) spectrum in the absence of added acid was the same whether the dissolved Fe(III) salt was the chloride, perchlorate or sulfate. Hence this spectrum was attributed to either the solvated species $Fe(HS)_n^{+3}$ of the solvent HS or to the solvolyzed species FeS^{+2} or to the aquo-ferric ion or to the $FeOH^{+2}$ ion in NMA. This spectrum was unchanged by the addition of water to the anhydrous solvent ($[H_2O] < 0.002$ *M*) up to water concentrations of 6 *M*. If water molecules are preferentially complexed by Fe^{+3} in NMA, then this spectrum quite possibly could be that of the aquo-ferric ion or of the hydrolyzed ferric ion, $FeOH^{+2}$. However, Fig. 3 shows that although this spectrum resembles that of $Fe(H_2O)_5(OH)^{+2}$ qualitatively, it is shifted to much longer wave lengths. The maximum at 295 mμ in the spectrum of the aquo-$FeOH^{+2}$ ion found here agrees very well with the maximum found by Olson and Simonson.[4] The corresponding maximum in NMA is at 350 mμ. This large shift would not be expected to result from solvent effect on the absorption of $Fe(H_2O)_5(OH)^{+2}$. If the observed absorption is the result of transitions of 3d-electrons between 3d-orbitals whose

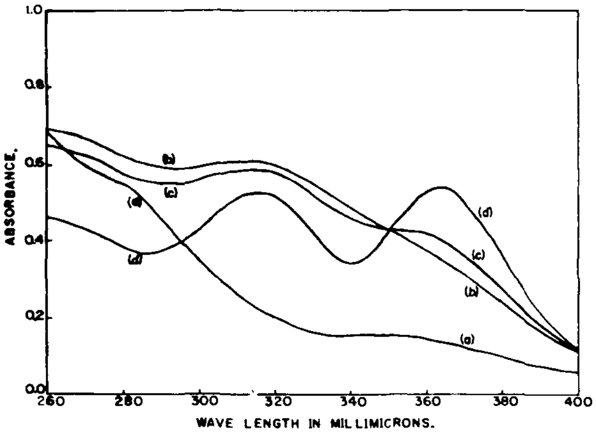

Fig. 2.—(a) 8 × 10^{-5} *M* $FeCl_3$, no acid added; (b) 7.4 × 10^{-5} *M* $FeCl_3$, 0.015 *M* HCl; (c) 7.4 × 10^{-5} *M* $FeCl_3$, 0.025 *M* HCl; (d) 7.4 × 10^{-5} *M* $FeCl_3$, 0.10 *M* HCl; cell length 1.00 cm.

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[2] Unpublished thesis research.

[3] Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., p. 285.

[4] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

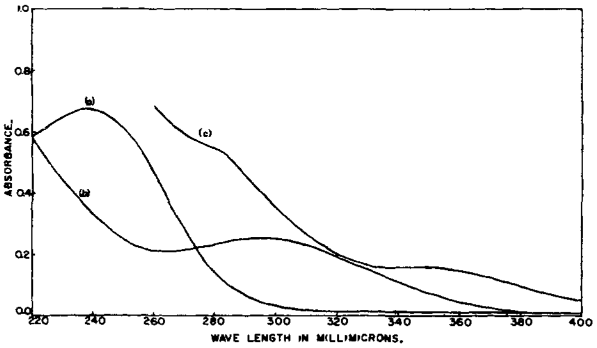

Fig. 3.—(a) 1.32×10^{-4} *M* Fe(III), 0.10 *M* $HClO_4$, water as solvent; (b) 1.32×10^{-4} *M* Fe(III), 0.001 *M* $HClO_4$, water as solvent; (c) 8×10^{-5} *M* Fe(III), no acid added, NMA as solvent.

energies have been separated by the ligand field effect, then the absorption spectrum is determined primarily by the nature and symmetry of the ligands and general solvent effect is only of secondary importance. Hence, it is probable that this spectrum is due to $Fe(HS)_n^{+3}$ or FeS^{+2} and more probably the latter. It was not possible to decide experimentally at this point between these two ions because addition of an acid, which would have repressed solvolysis, introduced an anion and caused complex formation between Fe^{+3} and the anion.

Determination of Extinction Coefficients and Complex Constants.—These equilibria were assumed to be present in the solutions studied

$$Fe^{+3} + HS = FeS^{+2} + H^+;\ K_S = \frac{[FeS^{+2}][H^+]}{[Fe^{+3}]} \quad (1)$$

$$Fe^{+3} + Cl^- = FeCl^{+2};\ K_1 = \frac{[FeCl^{+2}]}{[Fe^{+3}][Cl^-]} \quad (2)$$

$$FeCl^{+2} + Cl^- = FeCl_2^+;\ K_2 = \frac{[FeCl_2^+]}{[FeCl^{+2}][Cl^-]} \quad (3)$$

Two additional assumptions were made which are justified by the results obtained. First the molar extinction coefficient of the solvated Fe^{+3} ion was assumed to be negligible at 363 mμ. This assumption is not unreasonable in view of the fact that the hydrated Fe^{+3} ion does not absorb appreciably until wave lengths less than 300 mμ are used. Secondly, it was assumed that in the absence of added acid and at the Fe(III) concentrations employed the solvolysis of Fe^{+3} was virtually complete. This assumption permitted the determination of the molar extinction coefficient e_2 of FeS^{+2} by direct measurement of the absorption of a solution of known Fe(III) concentration; a value of 1790 l. mole^{-1} cm.$^{-1}$ was found for e_2.

In the presence of an excess of Cl^- the absorbance *A* of a solution in a 1.00-cm. cell was given by

$$\begin{aligned} A &= e_2[FeS^{+2}] + e_3[FeCl^{+2}] + e_4[FeCl_2^+] \\ &= \left\{\frac{(e_2K_S/[H^+]) + e_3K_1[Cl^-] + e_4K_1K_2[Cl^-]^2}{1 + (K_S/[H^+]) + K_1[Cl^-] + K_1K_2[Cl^-]^2}\right\}[FeIII] \quad (4) \\ &= \alpha[FeIII] \end{aligned}$$

where [FeIII] = $[Fe^{+3}] + [FeS^{+2}] + [FeCl^{+2}] + [FeCl_2^+]$ and α is a constant at given H^+ and Cl^- concentrations. The absorbance was proportional to the total iron concentration up to 1.34×10^{-4} *M*, the highest concentration employed, as may be seen from Fig. 4 for one particular set of H^+ and Cl^- concentrations.

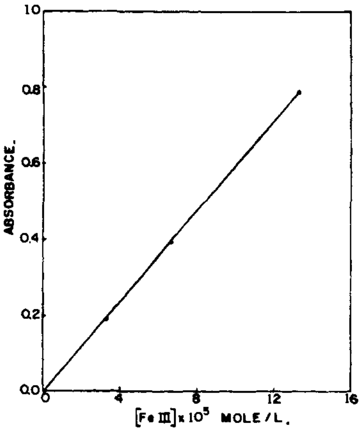

Fig. 4.—363 mμ; $[Cl^-] = 0.100$ *M*; $[H^+] = 0.025$ *M*; cell length 1.00 cm.

Values of α were found for five sets of H^+ and Cl^- concentrations, thus giving five equations which could be solved simultaneously for e_3, e_4, K_S, K_1 and K_2. The necessary data are given in Table I.

TABLE I

VALUES OF α, THE PROPORTIONALITY CONSTANT RELATING OPTICAL DENSITY AND TOTAL Fe(III) CONCENTRATION, AT VARIOUS $[H^+]$ AND $[Cl^-]$

e_2 = 1790 l. mole^{-1} cm.$^{-1}$; 30 ± 3°

$\alpha \times 10^{-3}$	$[H^+]$, mole/l.	$[Cl^-]$, mole/l.
1.24	0.0010	0.0010
1.28	.0020	.0020
1.79	.0050	.025
3.50	.025	.025
5.00	.025	.060

For the first three sets of data listed in Table I the last term in the numerator and denominator of α may be neglected. Thus these three sets of data yield values of 1890 l. mole^{-1} cm.$^{-1}$, 1.4×10^{-3} mole l.$^{-1}$ and 7.5×10^2 l. mole^{-1} for e_3, K_S and K_1, respectively. The last two sets of data yield values of 9.3×10^3 l. mole^{-1} cm.$^{-1}$ and 13 l. mole^{-1} for e_4 and K_2, respectively. These values of the constants were used to calculate a value for α for $[H^+] = 0.025$ *M* and $[Cl^-] = 0.100$ *M*. The calculated value was 5.97×10^3; the observed value was $(5.82 \pm 0.30) \times 10^3$, in good agreement with the calculated value.

The assumption concerning the virtually complete solvolysis of Fe^{+3} in the absence of added acid may now be examined. For [FeIII] = 6.7×10^{-5} *M* and $K_S = 1.4 \times 10^{-3}$ the concentration of FeS^{+2} may be calculated to be 6.5×10^{-5} *M*. Therefore the assumption was justified.

Furthermore the values of K_S, K_1 and K_2 are in agreement with the fact that the spectrum for Fe(III) in the presence 0.015 *M* HCl passed through the isosbestic point of Fig. 2 for the two higher HCl concentrations. A calculation shows that less than 8% of the Fe(III) in the solution containing 0.015 *M* HCl was present as Fe^{+3} and FeS^{+2}.

A smaller percentage than this would be found if K_2, determined from data at ionic strengths of 0.025 and 0.060, was corrected for the lower ionic strength of 0.015 involved here.

Ionic strength was not maintained at a constant value since it would have been impossible to do so over the range of H^+ and Cl^- concentrations employed without addition of other anions which would have introduced additional complexes.

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MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

Solution Viscosity Behavior of Some Metal Schiff Base Chelates

BY ROBERT G. CHARLES

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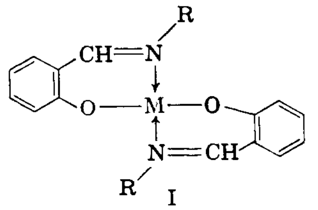
Viscosity measurements are suggested as useful adjuncts to other physical methods for the study of metal chelate compounds dissolved in organic solvents. In favorable instances such measurements can give information relative to the steric configuration of the dissolved molecules and to the degree and type of interaction of the solute molecules with the solvent. The viscosities of dilute solutions derived from the members of three homologous series of Cu(II), Ni(II) and Zn(II) N-(*n*-alkyl)-salicylaldimine chelates have been studied, using as solvents toluene, dioxane and pyridine. With the exceptions of the results obtained for the nickel chelates in pyridine the viscosity results ($\eta_{sp/c}$ as defined in the text) were found to be roughly independent of the solvent employed and of the nature of the bonded metal. The magnitude of $\eta_{sp/c}$ increased, however, with increasing chain length in all the solvents and for all three homologous series. Values of $\eta_{sp/c}$ for the nickel chelates in pyridine were higher than those for the corresponding Cu and Zn compounds due to the interaction of the nickel compound with the solvent to form hexacoördinated complexes. The values of $\eta_{sp/c}$ for the one copper compound studied having an enforced planar *cis* configuration about the metal were higher than those found for corresponding alkyl substituted chelates, evidently as the result of the permanent dipole moment associated with the *cis* configuration.

Solution viscosity measurements have been used but little in the study of metal coördination compounds. In an earlier paper[1] it was shown that significant information concerning the ethylenediaminetetraacetate chelates could be obtained by such measurements on aqueous solutions. It might be expected that, in favorable instances, useful information regarding the degree of solvation and the configuration of metal chelate compounds might be obtained also for solutions in organic solvents.

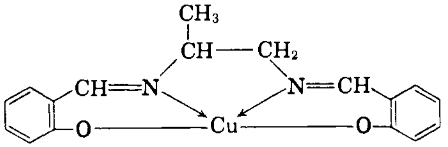
The present work is concerned largely with the N-(*n*-alkyl)-salicylaldimine chelates I, where R is a straight chain alkyl group and M is Cu, Ni or Zn.



I

We have chosen this group of compounds because of their adequate solubilities in organic solvents and, more particularly, because other data are available regarding the solution properties of some of these chelates.[2-7]

For comparison with the chelates I we have made a few measurements also with the copper chelate II, where the *cis* planar configuration about the metal atom is enforced by the N–N bridging group.



II

Experimental

Materials.—The preparation and properties of the N-alkylsalicylaldimine chelates have been described elsewhere.[2,3,8] All of these compounds were recrystallized and dried, *in vacuo*, over $CaCl_2$.

Bis-(salicylaldehyde)-propylenedimine-copper(II)[9] was prepared by condensing salicylaldehyde with propylenediamine in methanol solution and then reaction with copper acetate in the presence of sodium acetate. The yield was 97%. The violet compound was recrystallized from methanol and dried at room temperature in a vacuum desiccator; m.p. 238–243°. *Anal.* Calcd. for $C_{17}H_{16}O_2N_2Cu$: C, 59.4; H, 4.7; N, 8.2. Found: C, 59.2; H, 4.5; N, 7.9.

Carbide and Carbon 1,4-dioxane was purified by refluxing for 12 hr. over sodium and fractionating through an efficient column. Reagent grade pyridine and reagent grade toluene were used without additional purification.

Procedure.—Solutions were prepared by weighing the compound into a 10-ml. volumetric flask and diluting to volume with the solvent. All measurements were completed within a few hours of preparing the solutions.

Viscosities were determined with a Cannon–Fenske capillary viscometer having an efflux time greater than 200 seconds. Efflux times were determined with a stopwatch. Each solution was compared with the corresponding solvent run under the same conditions. All solvents and solutions were filtered through a sintered glass pressure filter before the viscosity runs were begun. Densities of solutions and solvents were determined concurrently with the viscosity measurements, using a 5-ml. Weld pycnometer. All determinations were made at 30° in a water-bath which could be maintained constant to ±0.01°.

Viscosities were calculated in the usual manner from the efflux times and densities. Results were expressed in Table

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(2) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(3) R. G. Charles, *J. Inorg. Nucl. Chem.*, accepted for publication.

(4) F. Basolo and W. R. Matoush, THIS JOURNAL, **75**, 5663 (1953).

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(7) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4062 (1957).

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(9) P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 81 (1933).